Trimethylsilylation of Inorganic Silicates

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The effect of time, temperature, and concentration of reactants on the formation of trimethylsilyl-derivatives of akermanite and β-dicalcium silicate has been studied.

A STUDY of the formation of trimethylsilyl orthosilicates (I) and pyrosilicates (II) is of interest because of the potential of the method of trimethylsilylation in (1) the study of the structure of silicates and (2) the preparation of new macromolecules derived from silicates.

$$\underset{\text{(I)}}{SiX_4} \qquad \underset{\text{(II)}}{(SiX_3)_2O} \qquad (X = Me_3SiO)$$

Trimethylsilyl silicates have been prepared by treating silicates with mixtures of water, hydrochloric acid, isopropyl alcohol, and hexamethyldisiloxane;[1] a detailed study of the treatment of hemimorphite under these conditions has been reported.[2] Trimethylsilyl-derivatives of chrysotile asbestos have also been prepared in this way.[3,4]

We describe here our application of this method to the pyro-compound akermanite ($Ca_2MgSi_2O_7$) and the ortho-compound β-dicalcium silicate (Ca_2SiO_4) in order to study the effect of variations of time, temperature, and concentration of reactants.

EXPERIMENTAL

Akermanite and β-dicalcium silicate were prepared at the Building Research Station, Watford, Herts; they were characterised by *X*-ray diffraction.

General Procedure.—The silicate (10 g), (100 mesh) was treated with the reagents under the reaction conditions listed in Tables 1—3. The mixtures were then filtered; the non-aqueous layer was separated, washed with water, dried (Na_2SO_4), and then examined by g.l.c.

Analysis by G.l.c.—The gas chromatograph used was a Perkin-Elmer F11 instrument. The 2 m by 3 mm column was packed with a methylsilicone gum rubber, SE 30,

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[1] C. W. Lentz, *Inorg. Chem.*, 1964, **3**, 574; C. W. Lentz, Special Report 90, Highway Research Board, Washington, D.C., 1966, 266; C. W. Lentz, Mag. Concrete Res., 1966, **18**, 231.

[2] J. Götz and C. R. Masson, *J. Chem. Soc.* (*A*), 1970, 2683.

[3] S. E. Frazier, J. A. Bedford, J. Hower, and M. E. Kenney, *Inorg. Chem.*, 1967, **6**, 1693.

[4] J. J. Fripiat and E. Mendelovici, *Bull. Soc. chim. France*, 1968, 483.

TABLE 1

Effect of variations in time on reaction products [a]

Silicate [b]	Reaction time (h)	% of total trimethyl-silylated products (I)	(II)	(I)/(II)
A	2	17·7	11·7	1·5
A	8	18·3	26·5	0·7
A	48	15·3	24·5	0·6
B	2	20·5	21·5	0·9
B	8	21·1	19·9	1·0
B	48	23·2	20·0	1·2

[a] Hexamethyldisiloxane (66·6 ml), ice (42 g), isopropyl alcohol (100 ml), and hydrochloric acid (d = 1·1878, 50 ml) were used, stirred for 1 h before addition of silicate (10 g); reaction temperature 25 °C. [b] A = Akermanite, B = β-dicalcium silicate.

TABLE 2

Effects of variations in temperature on reaction products [a]

Silicate [b]	Reaction temperature (°C)	% of total trimethyl-silylated products (I)	(II)	(III)	(I)/(II + III)
A	25	17·7	11·7	Trace	1·5
A	0	16·0	23·5	14·4 [c]	0·4
A	−25	12·2	27·8	29·2 [c]	0·2
B	25	20·5	21·5	Trace	0·9
B	0	27·5	12·9	6·5 [c]	1·4
B	−25	Trace	Trace	Trace	

[a] Hexamethyldisiloxane (66·6 ml), ice (42 g), isopropyl alcohol (100 ml), and hydrochloric acid (d = 1·1878, 50 ml) were stirred at the reaction temperature for 1 h before addition of the silicate (10 g). The reaction time in each case was 3 h. [b] A = Akermanite, B = β-dicalcium silicate. [c] These products were in each case converted to the fully trimethylsilylated Si_2O_7 derivative by shaking with Amberlyst 15 (a macroreticular large mesh strong acid cation-exchange resin).

absorbed on Celite 85—100 mesh. The column was kept at 50 °C for an initial period of 10 min after which the temperature was raised to 300 °C at 25° min^{-1}. The compounds detected were $(Me_3Si)_2O$ and $(Me_3Si)_4SiO_4$ at 50°; $(Me_3Si)_3Si_2O_6(Me_3Si)_2OH$ and $(Me_3Si)_6Si_2O_7$ at 230°; $(Me_3Si)_8Si_4O_{12}$ (cyclic) at 250°; $(Me_3Si)_8Si_3O_{10}$ at 280°; unknown >280°. Quantitative data was deduced from chromatograms by measuring peak areas.

Possible Rearrangement of Trimethylsilyl-derivatives.—To check on the possible rearrangement of trimethylsilyl-derivatives, either in the reaction or upon g.l.c. examination two mixtures were taken which, in addition to higher molecular-weight fractions, contained in one case, (I) (94%) and (II) (3%), and in the other case, (I) (5%) and (II) (54%). Each was shaken for 2 days at 25° with a mixture of hexamethyldisiloxane (13·3 ml), isopropyl alcohol (20 ml), hydrochloric acid (d = 1·18) (10 ml), and water (8·4 g). They were then worked and examined by g.l.c. No change in the relative proportions of the derivatives was noted.

DISCUSSION

Variation in Reaction Time (*Table* 1).—As reported for hemimorphite,[2] both akermanite and β-dicalcium silicate give mixtures of (I) and (II); the relative proportions vary with time but reach approximately constant values at times up to 8 h.

Variation in Temperature (*Table* 2).—Both compounds show a decrease in extent of reaction at lower temperatures and also a considerable increase in the derivative corresponding to the starting material. Götz–Masson reported similar results.[5] This behaviour parallels that for the rate of polymerisation of silicic acid [6] which decreases with decrease in temperature. At lower temperatures akermanite, gave rise to increasing amounts of the incompletely trimethylsilylated derivative (III).

$$X_3Si\cdot O\cdot SiX_2\cdot OH \quad (X = Me_3SiO)$$

(III)

The use of Amberlyst 15 achieved the conversion of (III) into (II).

TABLE 3

Effect of variations in reactants on reaction product [a]

Experiment	Silicate [b]	Water (ml)	HCl (d = 1·18) (ml)	$\mathrm{Pr^iOH}$ (ml)	Trichloroacetic acid (g)	Hexamethyldisiloxane (ml)	Trimethyl chlorosilane (ml)	% of total trimethyl-silylated products (I)	(II)	(I)/(II)
a	A	0	50	100	0	66·6	0	16·2	63·8	0·3
b	B	0	50	100	0	66·6	0	48·0	39·3	1·2
c	A [c]	42	50	0	0	66·6	0	Trace	Trace	
d	B [c]	42	50	0	0	66·6	0	Trace	Trace	
e	A [d]	42	20 [e]	100	0	66·6	0	Trace	Trace	
f	B [d]	42	17 [e]	100	0	66·6	0	Trace	Trace	
g	A [c]	50	0	100	21·3	66·6	0	Trace	Trace	
h	B [c]	50	0	100	21·3	66·6	0	Trace	Trace	
i	A	50	0	100	21·3	0	80	18·9	62·7	0·3
j	B	50	0	100	21·3	0	80	43·7	50·8	0·8
k	A [f]	0	50	250	0	0	100	11·0	47·6	0·2
l	B [g]	0	50	250	0	0	100	Trace	Trace	

[a] The reaction conditions were 3 h at 25 °C in each case. [b] A = Akermanite; B = β-dicalcium silicate. [c] Silica gel recovered. [d] Small quantity of silica gel and starting material recovered. [e] This amount of HCl was required to keep the pH at 2—3. [f] (2·6 g) Unreacted akermanite recovered. [g] (3·7 g) Unreacted β-dicalcium silicate recovered.

Variations in Reactants (*Table* 3).—Not only does aqueous hydrochloric acid bring the silicates into solution but also brings about rearrangement of the silicate anions. Thus, less water (a and b) gave products more representative of the original silicate structure.[5]

Isopropyl alcohol is used to make the reaction mixture homogeneous; it is known,[7] however, that siloxane

[5] J. Götz and C. R. Masson, *J. Chem. Soc.* (*A*), 1971, 686.

[6] S. A. Greenberg and D. Sinclair, *J. Phys. Chem.*, 1955, **59**, 435.

[7] C. Eaborn, ' Organosilicon Compounds,' Butterworths, London, 1960, 262.

rearrangements, readily occur in alcoholic and aqueous alcoholic solutions. The absence of isopropyl alcohol (c and d) gives what is thought to be silica gel, *i.e.* the silicate anions have been brought into aqueous solution and, in the absence of a trimethylsilylating species, they polymerise.

The hydrochloric acid also catalyses the breakdown of hexamethyldisiloxane to trimethylsilanol and trimethylchlorosilane, the latter being further hydrolysed to trimethylsilanol. Trimethylsilanol is presumably the active trimethylsilylating species.

$$Me_3SiOSiMe_3 + HCl \rightleftharpoons Me_3SiCl + Me_3SiOH +$$

$$Me_3SiCl + H_2O \rightleftharpoons Me_3SiOH + HCl$$

With only a little hydrochloric acid present (e and f) a small quantity of silica gel together with starting materials are recovered. Use of trichloroacetic acid (g and h) gives silica gel; no starting materials are recovered and no trimethylsilyl-derivatives are obtained. This is expected since trichloroacetic acid does not catalyse the breakdown of hexamethyldisiloxane.[8] If however, trichloroacetic acid is used (i and j) in combination with trimethylchlorosilane, *i.e.* no breakdown of hexamethyldisiloxane to give the trimethylsilylating agent is necessary, trimethylsilyl-derivatives are formed. Frazier *et al.*[3] used a reaction mixture containing trimethylchlorosilane in place of hexamethylchlorosilane. Application (k and l) of this technique to akermanite gives a relatively high yield of (II) but only trace quantities of (I) and (II) are obtained with β-dicalcium silicate.

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[8] C. Eaborn, 'Organosilicon Compounds,' Butterworths, London, 1960, 255.